

Kaunas University of Technology
Institute of Physical Electronic of
Kaunas University of Technology

Kristina Žukienė

**THE STRUCTURE OF MORPHOLOGY AND
PROPERTIES OF MODIFIED POLYCHLOROPRENE
ADHESIVE COMPOSITION**

Summary of doctoral dissertation

Technological Sciences, Materials Engineering (08 T)

Kaunas, 2004

The scientific work was carried out in 1998 - 2004 at Kaunas University of Technology, Faculty of Design and Technologies, supported by Lithuanian State Science and Studies Foundation.

Scientific supervisor:

Assoc. Prof. Dr. Virginija JANKAUSKAITĖ (Kaunas University of Technology, Technological Sciences, Materials Engineering – 08 T).

Council of Materials Engineering trend:

Prof. Dr. Habil. Juozas Vidas GRAŽULEVIČIUS (Kaunas University of Technology, Physical Sciences, Chemistry - 03 P);

Dr. Habil. Audronis Jonas KVIKLYS (Lithuanian Energy Institute, Technological Sciences, Materials Engineering - 08 T);

Assoc. Prof. Dr. Ričardas MAKUŠKA (Vilnius University, Physical Sciences, Chemistry - 03 P);

Prof. Dr. Habil. Vytautas Mykolas MILAŠIUS (Kaunas University of Technology, Technological Sciences, Materials Engineering - 08 T);

Prof. Dr. Habil. Sigitas TAMULEVIČIUS (Institute of Physical Electronics of Kaunas University of Technology, Technological Sciences, Materials Engineering - 08 T) – *chairman*.

Official opponents:

Dr. Rimantas LEVINSKAS (Lithuanian Energy Institute, Technological Sciences, Materials Engineering - 08 T);

Dr. Igoris PROSYČEVAS (Institute of Physical Electronics of Kaunas University of Technology, Technological Sciences, Materials Engineering - 08 T).

Public defence of the Dissertation will take place at the open meeting of the Council of Materials Engineering trend at 11 a.m. on 12 th. January 2005 in Dissertation Defence Hall at the Central Building of Kaunas University of Technology.

Address: K. Donelaičio g. 73 - 403, 44029, Kaunas, Lithuania.

Phone (370) 37 300042; Fax (370) 37 324144; e-mail mok.grupe@ktu.lt.

The sending-out date of the summary of the Dissertation is on 10 December, 2004.

The dissertation is available at the Libraries of Kaunas University of Technology (K. Donelaičio g. 20, Kaunas) and Institute of Physical Electronics of KTU (Savanorių pr. 271, Kaunas).

Kauno technologijos universitetas
KTU Fizikinės elektronikos institutas

Kristina Žukienė

**MODIFIKUOTŲ POLICHLORPRENINIŲ
ADHEZINIŲ KOMPOZICIJŲ STRUKTŪROS
MORFOLOGIJA IR SAVYBĖS**

Daktaro disertacijos santrauka

Technologijos mokslai, medžiagų inžinerija (08 T)

Kaunas, 2004

Disertacija rengta 1998 - 2004 metais Kauno technologijos universitete, Dizaino ir technologijų fakultete ir remta Lietuvos valstybinio mokslo ir studijų fondo.

Mokslinė vadovė:

Doc. dr. Virginija JANKAUSKAITĖ (Kauno technologijos universitetas, technologijos mokslai, medžiagų inžinerija - 08 T).

Medžiagų inžinerijos mokslo krypties taryba:

Prof. habil. dr. Juozas Vidas GRAŽULEVIČIUS (Kauno technologijos universitetas, fiziniai mokslai, chemija – 03 P);

Habil. dr. Audronis Jonas KVIKLYS (Lietuvos energetikos institutas, technologijos mokslai, medžiagų inžinerija - 08 T);

Doc. dr. Ričardas MAKUŠKA (Vilniaus universitetas, fiziniai mokslai, chemija - 03 P);

Prof. habil. dr. Vytautas Mykolas MILAŠIUS (Kauno technologijos universitetas, technologijos mokslai, medžiagų inžinerija - 08 T);

Prof. habil. dr. Sigitas TAMULEVIČIUS (Kauno technologijos universiteto Fizikinės elektronikos institutas, technologijos mokslai, medžiagų inžinerija - 08 T) – ***pirmininkas***.

Oficialieji oponentai:

Dr. Rimantas LEVINSKAS (Lietuvos energetikos institutas, technologijos mokslai, medžiagų inžinerija - 08 T);

Dr. Igoris PROSYČEVAS (Kauno technologijos universiteto Fizikinės elektronikos institutas, technologijos mokslai, medžiagų inžinerija - 08 T).

Disertacija ginama viešame Medžiagų inžinerijos mokslo krypties tarybos posėdyje 2005 m. sausio 12 d., 11 val. Kauno technologijos universiteto centrinių rūmų Disertacijų gynimo salėje.

Adresas: K. Donelaičio g. 73 - 403, 44029, Kaunas, Lietuva.

Tel. (370) 3 300042; Faksas (370) 37 324144; el. paštas

mok_grupe@ktu.lt

Disertacijos santrauka išsiųsta 2004 m. gruodžio 10 d.

Su disertacija galima susipažinti Kauno technologijos universiteto (K. Donelaičio g. 20, Kaunas) ir Kauno technologijos universiteto Fizikinės elektronikos instituto (Savanorių pr. 271, Kaunas) bibliotekose.

Introduction

Relevance of the research. The main reason of the growth of polymer blends study – they are widely used into variety applications. Properties of polymer blends are rarely simple averages of the components. However, some polymer combinations may exhibit more desirable properties than the parent polymers; this is the synergism of polymer blending. In the early stages the tremendous efforts were made to obtain homogeneous polymer blends. In modern technology, the great advantages are offered to heterogeneous blends with varying phase-separated structures. The type and dimensions of the morphology determine the properties of blend. Therefore, relationship between morphology and properties of polymer blend is paramount in both research and development and production, also.

The study of heterogeneous polymer system surface and interphase properties have been growing intensively, because of they important role in morphology. These investigations allow to control processes, for which properties and structure of boundary layers are essential.

The goal of the dissertation was to investigate the peculiarity of morphological changes of the modified polychloroprene adhesive in the aim to predict the mechanical and adhesive behaviour and to produce composition with useful and essential properties.

The objectives of the research are the following:

- to improve the adhesion properties of the polychloroprene adhesive by blending various polymeric additives;
- to investigate rheological behaviour of modified polychloroprene adhesive;
- to evaluate relationship between structure and properties of modified polychloroprene adhesive;
- to determine the influence of the surface properties of polymeric additives on the adhesion properties and structure of polychloroprene composition;
- to estimate the miscibility level and intermolecular interaction between polymers and to determine its influence on the polychloroprene adhesive properties.

Scientific novelty of the dissertation. Effective way to modify adhesion properties of composition is blending of different nature polymeric additives. As our investigations have shown, vinyl esters of versatic acids derivatives, piperylene styrene copolymer, poly(methyl methacrylate), izoprene or butadiene-nitrile rubbers can change polychloroprene adhesive properties.

The obtained data provide required information about the relationship between morphology and properties of the modified solvent-based polychloroprene adhesive composition:

- the viscosity data of pure polymers was used to analyze the phase behavior of blends;
- the development of morphology of immiscible non-Newtonian polymer-polymer dispersions has been analyzed using the models of the breakup and coalescence phenomena together with the rheological data. The relationship between particles sizes, concentration and viscosity ratio has been determined;
- the surface tension values of polymers films, obtained by experimental and theoretical methods, have been compared in order to obtain the right surface tension values;
- the improvement of polychloroprene adhesion properties by different surface properties polymeric additives has been estimated;
- the interaction between composition phases and compatibility on the adhesive properties has been investigated.

The obtained results can be used for the prediction and optimization adhesion properties of other polymer compositions. The investigations are important not only from technological but also from the scientific points of the view.

Approbation of the research results. The results of the research were presented in the 7 scientific publications.

Structure of the dissertation. This dissertation consists of: introduction, four chapters, conclusions, list of references (200 entries) and list of scientific publications. The materials of the dissertation are presented in 109 pages, including 64 figures and 24 tables.

Content of the dissertation

Introduction presents the relevance of the research, definition of the research aim and objectives, survey of the scientific novelty and practical value of the dissertation.

Chapter 1. Literature review gives the view of relevant publications related to the theme of dissertation. Thermodynamic as well as kinetic aspects of structure and morphology control of polymer blends were described. Also in this chapter discussion of the compatibility of blends and factors affecting them was presented. The importance of surface or interphase phenomenon for the final properties of blends is described.

Chapter 2 presents materials and methods of investigations. Chapter covers synthesis of polymers, molecular weights and measurements of glass transition temperatures. The mechanical properties tests, steady shear viscometric measurements of polymers solutions and measurements of peel strength of adhesive joints are included, also. The methods for characterization of surface composition and structure of polymers films, such as contact angle goniometry and atomic force microscopy, are presented.

Table 1 summarizes the molecular weights and glass transition temperatures of materials to be used for investigations.

Table 1. Characterization of materials used for investigation

Polymer	Molecular weight $M_w \cdot 10^3$	Glass transition temperature $T_g, ^\circ\text{C}$
Polychloroprene (PCP)	300	-45
Veova-10 I	160	-3
Veova-10 II	140	-3
Veova-10 III	132	-3
Veova-11/methyl methacrylate/2-ethylhexyl acrylate copolymer (Veova-11/MMA/2EHA)	100858	-11
Veova 10/vinyl acetate copolymer (Veova-10/VAc)	596	22
piperylene-styrene copolymer (PSC)	35	55

In **Chapter 3** is shown that various polymeric additives can modify structure, adhesion, mechanical and rheological properties of solvent-based polychloroprene adhesive. The properties of modified adhesive depend on the content, structure and nature of additives and are related to morphology and interaction between composition phases.

Influence of vinyl esters of versatic acids derivatives (Veova). Copolymers, such as Veova-11/MMA/2EHA and Veova-10/VAc (the weight ratios was 60/30/10 and 35/65, respectively) improve the properties of polychloroprene adhesive. It was defined that effective content of Veova copolymers leads to significant changes of PCP rheological behaviour. The viscosity of modified PCP depends on the shear rate, temperature, type of copolymer and interaction between composition phases.

Shear thinning index (STI) was used to evaluate the pseudoplastic behaviour of modified adhesive. It was found that pseudoplasticity increases, when copolymers content increases. Meanwhile, pseudoplasticity of unmodified PCP adhesives is significantly lower than those of the copolymers.

The viscosity of modified PCP was described by the additivity rule:

$$\log \eta_{12} = \phi_1 \log \eta_1 + \phi_2 \log \eta_2 \quad (1)$$

where ϕ_1 , ϕ_2 are the volume fractions of the two phases, η_{12} , η_1 or η_2 – shear viscosities of the blend and the two phases, respectively. The negative departure of the viscosity–composition relationship from the log-additivity rule of PCP modified by Veova-10/VAc was found at all composition range (Fig. 1). Therefore, it determines that blend is thermodynamically immiscible and form two phase structure.

It was found that an interrelationship between the structure and rheological properties of the blend exist. The sharp minimum of the viscosity of PCP at the 1 wt% of Veova-10/VAc, may correspond to the spontaneously formation of

dispersion, in which the particle sizes are very small. Owing to small size of the particles and low interaction between two phases in a given region of composition, there exists a highly developed interfacial surface with low intermolecular interaction. It confirms micrographs of this blends (Fig. 2 a). It is evident that blend consists of VeoVa-10/VAc domains dispersed in PCP matrix when amount of copolymer is held at 3 wt%. Size of particles ranges from 0.5 μm up to 2.0 μm .

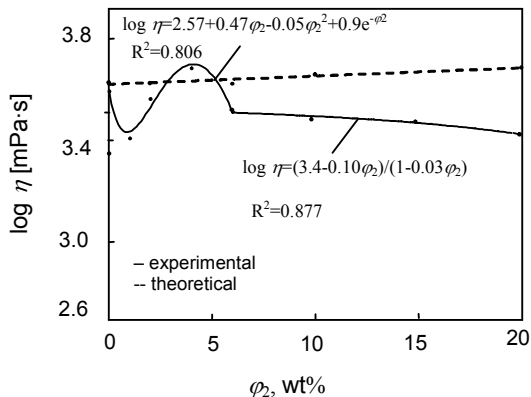


Fig. 1. Viscosity as a function of VeoVa-10/VAc content in PCP adhesive at shear rate $\dot{\gamma} = 13.7 \text{ s}^{-1}$

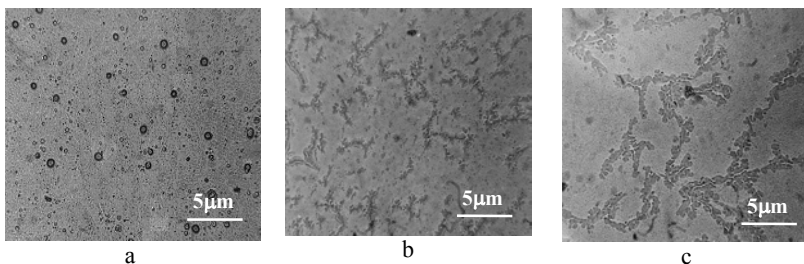


Fig. 2. Morphology of modified PCP adhesive films at different VeoVa-10/VAc content, wt%: a – 3; b – 4; c – 6

As VeoVa-10/VAc content is about 4 wt%, the size of particles and interaction between phases increase, indicating the increase of PCP viscosity (Fig. 2 b). Meanwhile, the further increase of the copolymer content causes the formation of inversion structure of adhesive (Fig. 2 c) and viscosity of PCP decreases (Fig. 1).

It was found that viscosity of VeoVa-11/MMA/2EHA modified PCP adhesive is above the log-additivity curves at all investigated composition

range (Fig. 3). In this case 10-15 wt% of the copolymer increases viscosity in 65-85%. From Fig. 4 it is evident that at 3 wt% of VeoVa-11/MMA/2EHA suspension structure is obtained – disperse phase in the matrix is dispersed in the form of different sizes spherical droplets. The size of domains grows when content of additive increases and boundary between the phases has high brightness. It may be assumed that these morphological changes cause significant increase in the viscosity of modified PCP adhesive.

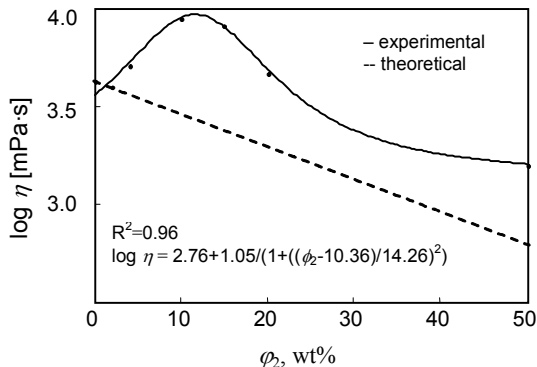


Fig. 3. Viscosity as a function of VeoVa-11/MMA/2EHA content in PCP adhesive at shear rate $\dot{\gamma} = 4.86 \text{ s}^{-1}$

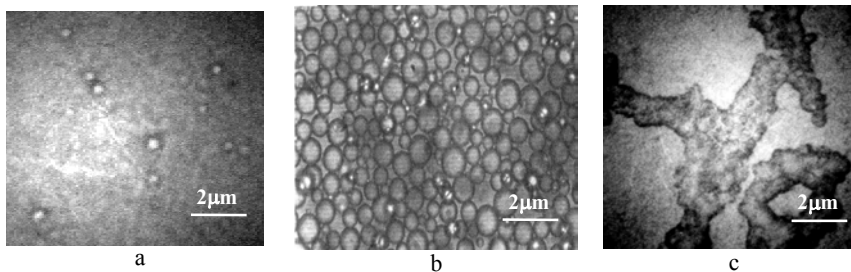


Fig. 4. Morphology of modified PCP adhesive films at different VeoVa-11/MMA/2EHA copolymer content, wt%: a – 3; b – 15; c – 35

Higher amount of copolymer exhibits polymer separation, formation of inversion structure of the blend and decrease in adhesive viscosity (Fig. 3 and Fig. 4).

Whereas properties of blends of immiscible polymers depend on the phase morphology, it is important to study the relationship between polymer characteristics, processing condition, blend composition and composition structure. During flow a structure of composition was investigated as a result of break-up and/or coalescence of dispersed particles. The state of particles

depends on the viscosity ratio λ ($\lambda = \eta_2 / \eta_1$, η_2 and η_1 – the viscosities of dispersed and continuous phases) and capillary number Ca ($Ca = \eta_1 \dot{\gamma} / \gamma_{12}$, r – the particles radius, $\dot{\gamma}$ – the shear rate, γ_{12} – the interfacial tension). The demarcation between the stable and unstable states of particle can be expressed by the critical capillary number Ca_{crit} ($Ca_{crit} = 0.05\lambda^{-2/3}$). If capillary number exceeds the critical value $Ca > Ca_{crit}$ the particles burst.

Veova-11/MMA/2EHA particles distribution in PCP adhesive as a function of the copolymer content is shown in Figure 5. It was found that particles distribution curves have distinct maximum, the position of which changes in the dependence of the copolymer content. The increase of the copolymer causes the curves maximum shift to the side of larger particles radius (from $r=0.5\ \mu\text{m}$ to $r=2.5\ \mu\text{m}$). Investigations show that similar processes proceed when time after blend homogenization increases. It may be related to the both particles coalescence during solution mixing and solvent evaporation processes. The coalescence in the blend with 3 wt% of the copolymer is negligible compare to that of the blend with higher Veova-11/MMA/2EHA content. It can be confirmed by average particles radius – it increases when time after homogenization increases.

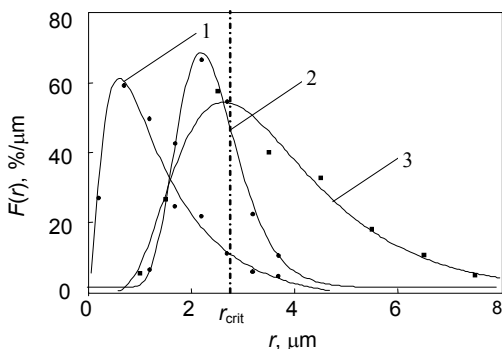


Fig. 5. The differential distribution curves of Veova-11/MMA/2EHA particles as a function of copolymer content, wt %: 1 – 3; 2 – 10; 3 – 20

The estimated critical value of the capillary number for Veova-11/MMA/2EHA particles in PCP matrices is $Ca_{crit} = 0.59$, at the viscosity ratio of $\lambda = 0.02$ (λ was determined at 20°C and $\dot{\gamma} = 145.8\ \text{s}^{-1}$). So, particles with radii higher than $1.5\ \mu\text{m}$ exceed the critical value $Ca > Ca_{crit}$ and burst. The vertical dashed line indicates the particles radius ($r = 2.8\ \mu\text{m}$), which is large enough to make the capillary number exceed the critical value (Fig. 5). It is evident that at low copolymer content (3 wt%) main part of particles radii are lower than $2.8\ \mu\text{m}$ and, so, are in the stable state (no break-up). On the other

hand, the vertical lines correspond to the distribution curves maximum, when the copolymer content increases up to 20 wt%. It indicates that most of disperse phase particles are formed by break up processes.

The investigations show that the evolution of the particles size distribution function depends on the viscosity ratio λ . VeoVa-10/VAc particles are higher than those of VeoVa-11/MMA/2EHA due to different viscosity at the same content. Therefore, the distribution of drop sizes narrows when viscosity ratio λ decreases from 0.26 (VeoVa-10/VAc) to 0.02 (VeoVa-11/MMA/2EHA).

The changes in morphology cause the changes in PCP adhesion properties upon VeoVa copolymers content. As can be seen from the Figure 6, low amount of VeoVa-10/VAc improves PCP adhesion strength in 30%. The influence of VeoVa-11/MMA/2EHA copolymer is significantly higher – in this case the peel strength increases in 68%. This can be referred to the high interaction in boundary of two polymer phases.

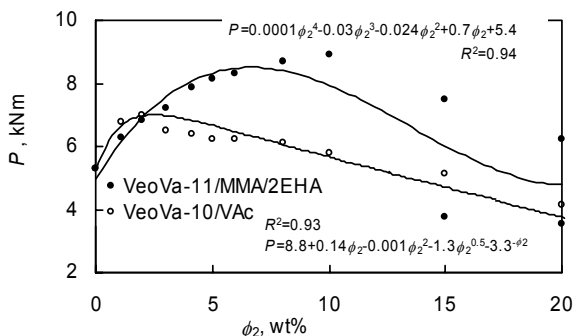


Fig. 6. Effect of VeoVa copolymers type and content on PCP adhesion properties (for styrene-butadiene rubber–canvas adhesive joints)

At higher VeoVa copolymers content peel strength decreases. It may be attributed to the decrease of composition cohesive strength due to the formation of inversion structure and decrease of interaction at the phases boundary.

On the other hand, different molecular weight VeoVa-10 polymers do not affect the bonding strength significantly. Only slight improvement of peel adhesion is achieved when VeoVa-10 polymers are blended. The effectiveness of polymers increases when their molecular weight decreases.

The changes in the adhesion properties were accompanied by the changes in the modified PCP adhesive mechanical properties. It was found that the influence of VeoVa-10/VAc copolymer on Young's modulus E_Y of adhesive film is negligible. On the other hand, 3-10 wt% of VeoVa-11/MMA/2EHA strengthens PCP adhesive film: E_Y in ~30%.

However, VeoVa copolymers produce same decrease in the deformability of the modified adhesive films. It is related to low mechanical strength of the copolymers comparing to that of PCP.

The influence of VeoVa-10 polymers on the mechanical properties of PCP adhesive is not remarkable and depends on the molecular weight.

Influence of piperylene styrene copolymer (PSC). The PCP/PSC compositions were investigated to determine the influence of the copolymer content on the phase morphology and rheological properties of the adhesive. Rheological measurements, performed at various temperatures, different copolymer content and adhesive solid content, show that the effect of shear rate is more significant in the systems with high solid content and with 25 - 30 wt% of PSC. Also, the influence of temperature is revealed more intensively, when PSC content is not less than 25 wt%. This content of copolymer results on appreciable decreases of the PCP adhesive viscosity.

The departure of the viscosity–composition relationship from log-additivity rule of PCP modified by PSC was found at all composition range. The viscosity of PCP adhesive with 15 - 25 wt% of PSC is above the log additive rule, indicating high interaction between phases. However, drastic decrease in the adhesive viscosity and, thus, negative departure of $\log\eta(\phi_2)$ relationship from the log-additivity rule was obtained for the blend with higher copolymer content.

Influence of isoprene or butadiene - nitrile rubbers and poly(methyl methacrylate). The improvement of PCP adhesion properties can be achieved by addition of poly(methyl methacrylate) (PMMA), isoprene rubber (SKI-3S) and butadiene-nitrile rubbers, also. The low amounts (1 - 4 wt.%) of PMMA or SKI-3S increase the peel strength of PCP adhesive in 28 - 31 %. The influence of butadiene-nitrile rubbers (SKN) is not such remarkable and depends on the number of acrylonitrile groups. Rubber with high amount of acrylonitrile is more effective.

In **Chapter 4** the surface structures arising in the polychloroprene adhesive composition was analyzed. The emphasis on the relationship between the adhesion properties and surface structure of adhesive film was made.

Surface tension of PCP, VeoVa derivatives and PSC films was estimated theoretically and defined by experimental contact angle techniques. It was obtained that the disparities between surface tension γ_s values of investigated polymers determined by different estimation methods are, with a few exceptions, very small. However, advantages and disadvantages are characteristic for each method to be used. Therefore, it is important to apply several independent methods in order to determine the real surface tension values.

Applied experimental methods are based on the contact angle measurements. Zisman method and four thermodynamic models – equation of

state (ES), Lifshitz-van der Waals acid-base (LWAB), geometric mean (GME) and harmonic mean (HME) approaches – were applied for polymers surface analysis. As can be seen from the Table 2, γ_s values from most approaches have high correlation. However, surface tension values of polymers depend on the liquids to be used or composition of liquids pairs.

Table 2. Comparison of investigated polymers films surface tensions γ_s (mJ/m²) from different estimation approaches

Polymers	Fowkes equation				LWAB	ES
	GME		HMA			
	W-DI	G-DI	W-DI	G-DI	W-G-DI	G
PCP	40.2	39.2	47.3	41.6	40.1	35.5
Veova-10/VAc	36.6	36.5	41.2	39.4	37.5	34.9
Veova-11/MMA/2EHA	37.2	37.1	40.7	39.1	37.7	33.0
Veova-10 II	27.7	26.9	33.5	30.7	28.5	33.8
Veova-10 I	37.3	35.5	43.7	39.0	37.9	41.8
PSC	48.5	47.6	53.9	49.5	48.8	39.4

W – water, G – glycerol, DI – diiodomethane,

Estimated values for γ_s of PCP are close to the values found in other author works. Veova polymers and copolymers surfaces have low energy. On the other hand, PSC has the higher γ_s value than most polymeric materials.

The theoretical estimation of surface tensions γ_s from both parachor P_s and cohesive energy E_{coh} , using the concept of molecular group contribution, was carried out, also. In this case γ_s values of estimated polymers are in a relatively good correlation with the experimental data. However, theoretical methods are not suitable for the evaluation of surface tension for polymers of the same nature, but different molecular weight.

The study of influence of surface properties of polymeric additives on PCP surface properties shows that its surface tension decreases as content of Veova-10 II increases. Low amount (3 wt%) of the additive reduces surface tension of PCP film from 41.0 mJ/m² up to 37.9 mJ/m² (Fig. 7). Further increase of Veova-10 II content does not make significant influence on the adhesive γ_s . It may be supposed that low surface tension Veova-10 II polymer has tendency migrate to the surface and enrich top layer of PCP. So, the excess of Veova-10 II on the adhesive surface decreases PCP adhesion properties due to low cohesion strength of the additive.

It was found that no direct correlation between surface tension of the modified adhesive and Veova copolymers content exists. So, in this case the improvement of PCP adhesion properties can not be explained only by surface tension data.

PCP surface tension depends on PSC content, also (Fig. 8). In this case 10-15 wt% of PSC increase γ_s of adhesive up to 44.9-46.9 mJ/m². However, surface tension decreases and becomes similar to that of unmodified adhesive at the higher PSC content. It may be supposed that high differences in surface tension values between blend components favour blend phase separation due to system tendency to minimize its total free energy.

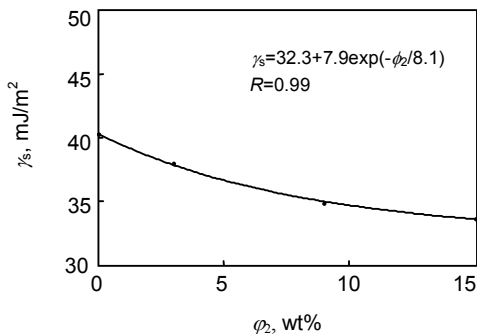


Fig. 7. Dependence of surface tension γ_s of PCP film on VeoVa-10 II polymer content

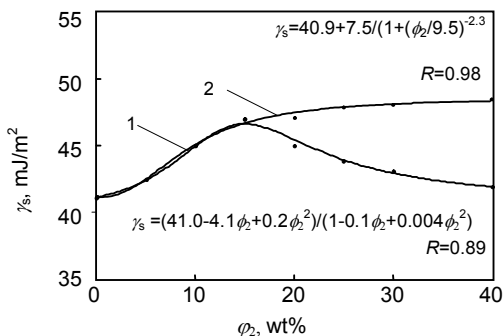


Fig. 8. Dependence of surface tension γ_s of PCP film top (1) and bottom (2) on the PSC content

To describe the mechanism of surface tension changes, the contact angles on the side of the PSC/PCP film facing the support (bottom of the film) were determined. The study has shown that up to 15 wt% of PSC surface tension is the same on both sides – film top and bottom. However, at the higher additive content γ_s of the top layer decreases, while of the bottom – increases and at 40 wt% of copolymer becomes similar to that of pure PSC. It may be concluded that up to 15 wt% of PSC composition is compatible. However, higher amount of PSC exhibits phases separation. The change of the composition surface state

may be attributed to the segregation of film, e.i. PCP segregated on the surface, PSC – on the bottom of film. It may be assumed that surface segregation is caused by the difference in surface tension between the components.

The phase separation causes the increase in the adhesion strength of styrene-butadiene-styrene thermoplastic (SBS) rubber joints. It is related to the increase of compatibility between SBS rubber and modified adhesive due to enrichment of adhesive bottom layer by PSC. It may be supposed that PSC acts as primer and intensifies interaction at the interface with rubber.

The different influence of the additives on the PCP surface properties can be related with compatibility between composition phases. For estimation of the compatibility the interfacial tension $\gamma_{s_1s_2}$ between adhesive components has been evaluated. It was found that most of studied additives are compatible with PCP, i.e. interfacial tension between the components is $\gamma_{s_1s_2} < 2 \text{ mJ/m}^2$.

Dilute-solution viscometry was applied to evaluate the compatibility between PCP adhesive components, also. This method is based on the determination of intermolecular interaction between the two different polymers in solution. The interaction between molecules leads to its conformational changes and, thus, influence on the solution viscosity.

The estimation of the compatibility of polymers in solvent-polymer-polymer system has been studied by means of four miscibility parameters: the signs of $\Delta[\eta]$, Δb , ΔB and thermodynamic parameter α . It is acceptable that polymer are miscible when experimental values of parameters are higher than that of theoretical (calculated from the weight additive rules) and immiscible – when lower.

It was found that PCP is immiscible with VeoVa-11/MMA/2EHA in all the composition range. It may be attributed to the presence of repulsive forces between polymers macromolecules. The miscibility parameters evaluated for the modified PCP compositions with VeoVa-10 III polymer indicate that these polymers are miscible in certain compositions. Both the attractive and repulsive interactions are characteristic for these blends. The miscibility limit is reached in the composition with 15 wt% of VeoVa polymer.

Meanwhile, the positive parameters values indicate that PCP and PSC are miscible for all adhesive composition range due to attractive interactions between polymers macromolecules.

The effect of the compatibility and polymers ratio on the surface morphology of PCP/PSC film was investigated by AFM. From AFM torsion images can be seen (Fig. 9) that films of pure PCP and PSC display different images. Single PCP contains a large number of hills and valleys (Fig. 9 a). On the other hand PSC film exhibit flat surface (Fig. 9 b). These differences can be attributed to the difference in molecular weight and structure of polymers.

The surface of PCP/PSC film shows torsion images different from that of the pure polymers. Addition of 15 wt% of PSC causes the formation of fine structure, but with higher local surface height. From Fig. 10 it is evident that composition surface consisted of bright and dark areas. It may be assumed that bright areas, which occupied the largest area of the image, correspond to PCP phase and dark areas – to PSC phase. Therefore, the composition has two phase structure.

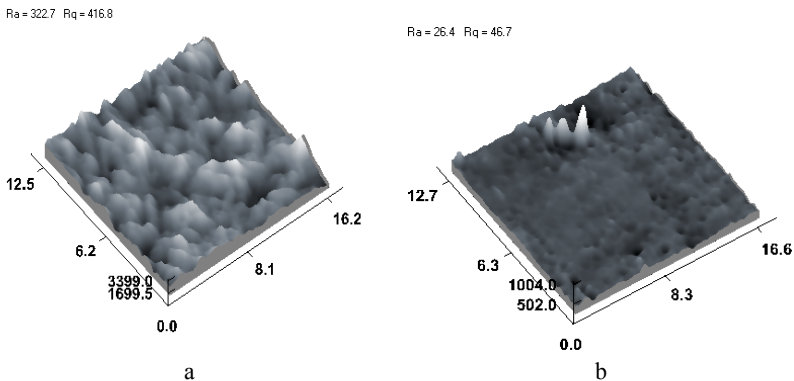


Fig. 9. AFM torsion images of PCP (a) and PSC (b) films top

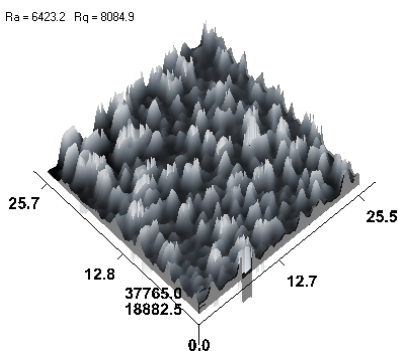


Fig. 10. AFM torsion image of PCP–PSC (85/15 wt%) film top

In order to confirm the segregation effect of the adhesive with 25 wt% and 40 wt% of PSC, that was described above, the torsion images of films top and bottom were compared (Fig. 11). AS can be seen, the top and bottom of modified PCP films display distinct AFM images. The top of film exhibits the images like that of pure PCP, while the surface of bottom layer has lower roughness, its torsion images just like that pure PSC.

Ra = 215.5 Rq = 282.7

Ra = 135.6 Rq = 172.6

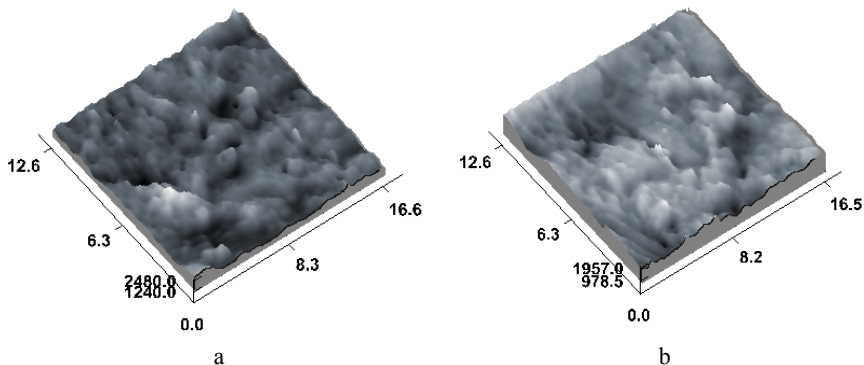


Fig. 11. AFM torsion images of PCP/PSC (60/40 wt%) film top (a) and bottom (b)

Thus, the modification of PCP adhesive by vinyl ester and styrene additives allows to manipulate its surface properties. However, it is not easy to explain synergism of adhesion properties by the changes in the surface properties of the binary blend or single blend components. The process of adhesion is complex and may involve several different mechanisms. The combination of these individual contributions leads to the final strength of adhesive joints, though individual mechanisms may dominate under specific conditions.

Conclusion

1. Polymer additives, such as vinyl esters of versatic acids derivatives (Veova), piperylene-styrene copolymer (PSC), poly(methyl methacrylate), izoprene or butadiene-nitrile rubbers can be used for solvent-base polychloroprene adhesive modification. Synergetic effect is characteristic for the modified adhesive, the degree of which depends on the type and content of additives.
2. Veova copolymers show the greatest influence on the properties of polychloroprene adhesive. Effective content of copolymers increases viscosity, mechanical and adhesion properties in 30 % and 70 %, respectively. It can be referred to high interaction energy and compatibility between composition phases.
3. It was found that an interrelationship between the morphology and rheological properties of the modified PCP adhesive exists. The changes in the PCP solution viscosity correspond to the spontaneous changes of adhesive structure. The decrease of viscosity at low copolymers content (1-2 wt%) corresponds to the forming suspension structure. In this case Veova copolymers particles are dispersed in polychloroprene matrices. The increase of copolymers content (up to 5 - 15 wt%), leads to the increase of particles size, interaction between phases and adhesive

- viscosity. Higher amount of copolymers exhibits formation of continuous two phase structure (inversion structure) and decrease in adhesive viscosity.
4. The structure of VeoVa copolymers the modified polychloroprene adhesive film depends on the microrheological processes during components blending and adhesive film formation. The size of copolymers particles is determined by both break-up and coalescence processes. The demarcation between the stable and unstable state of the particles was defined by the value of critical capillary number. It was found that at the lower VeoVa content (3 wt%) average radius of the particles remains constant and do not exceed the critical value. At the higher content – coalescence and break-up of VeoVa particles takes place simultaneously, therefore polydispersity and particles radius increase.
 5. The surface tension values of PCP and its modifiers films were obtained by experimental and theoretical methods. It was found that VeoVa polymers and copolymers have low energy surfaces. PSC has the higher surface tension value than most polymeric materials. The surface tensions, estimated by experimental methods, based on the contact angle measurements, are dependent on the liquids to be used for determination and experimental errors of measurements. The theoretical estimation of surface tensions from parachor and cohesive energy, using the concept of molecular group contribution, are not suitable for the evaluation of surface tension for different molecular weight of VeoVa polymers.
 6. The study of surface tension and surface morphology by atomic force microscopy shows that surface tension of polymeric additives has the significant influence on the structure and adhesion properties of polychloroprene adhesive:
 - low surface tension VeoVa polymer has tendency to migrate to the surface and to enrich top layer of polychloroprene. The increase of the excess of modifier on the adhesive film surface decrease peel strength of adhesive joints due to the low cohesion strength of additive;
 - the influence of VeoVa copolymers, which have similar surface tension as polychloroprene, on the surface properties of composition are negligible;
 - the enrichment of adhesive bottom layer by the additive occurs using high surface tension piperylene-styrene copolymer. In this case the adhesion properties of polychloroprene depend on the additive compatibility with substrate to be bonded.
 7. The miscibility behaviour of the modified polychloroprene composition was studied by the determination of the polymers interaction parameters, using dilute-solution viscometry method. It was found:

- PCP is immiscible with VeoVa-11/MMA/2EHA in the all composition ranges. It may be attributed to repulsive forces between polymers macromolecules;
 - PCP is miscible with VeoVa-10 polymer only at the higher modifier content (9 - 15 wt%). Both the attractive and repulsive interactions was established in this case;
 - the positive parameters values in all compositions range indicate the attractive interactions between PCP and PSC. So, miscibility between these components is characteristic.
8. Investigation show that surface tension values can be used for the screening suitable polymers pairs for the blends. The knowledge of surface tension of adhesive components is essential to the prediction of compatibility, structure development and performance characteristic of adhesive compositions.

List of Publication and Proceedings

Publications Corresponding to the List of Lithuanian Department of Science and Education

1. Fataraitė, E., Jankauskaitė, V., Žukienė, K., Tamošiūnas, J. Rubber Modified Adhesive Compositions *Materials science (Medžiagotyra)* ISSN 1392-1320 2 (7) 1998: pp. 73-77.
2. Barkauskas, R., Jankauskaitė, V., Mickus, K. V., Žukienė, K. Rheological Behaviour of Polychloroprene Adhesives Modified by Piperylene-Styrene Copolymer. *Materials science (Medžiagotyra)* ISSN 1392-1320 3 (5) 1999: pp. 22-27.
3. Jankauskaitė, V., Barkauskas, R., Mickus, K. V., Žukienė, K. Concentration Effect on the Rheology of Polychloroprene/Piperylene-Styrene copolymer solutions *Applied Mechanics and Engineering* 4 ISSN 1425-1655 1999: pp. 221-226.
4. Žukienė, K., Jankauskaitė, V., Railaitė, A. Structure and Properties of Vinyl Derivatives Modified Polychloroprene Adhesive. *Materials science (Medžiagotyra)* ISSN 1392-1320 3 (6) 2000: pp.193-198.
5. Žukienė, K., Jankauskaitė, V., Buika, G., Petraitiienė, S. Experimental and Theoretical Estimation of Surface Tension for Polychloroprene and VeoVa polymers. *Materials Science (Medžiagotyra)* ISSN 1392-1320 3 (8) 2002: pp. 266-267.
6. Žukienė, K., Jankauskaitė, V. Viscometric Study on the Compatibility of Polychloroprene and Vinyl Derivatives Blends in Solution. *Material Science (Medžiagotyra)* ISSN 1392-1320 4 (8) 2002: pp. 442-447.
7. Žukienė, K., Jankauskaitė, V. Surface properties and structure of modified polychloroprene adhesive for footwear production. *Projektowanie*,

materialy, technologia skory, odziezy i obuwi ISSN 0860-9241 21 2002: pp.146-150.

Referred Proceedings of International Conferences

1. Žukienė, K., Jankauskaitė, V. Properties of Polychloroprene Adhesive Modified with Vinyl Ester. In: *Baltic Textile & Leather*, ed.: Proceedings of International conference, Kaunas-Vilnius, September 11-12, 2003: pp. 216-221.

Proceedings and Theses of Lithuanian and International Conferences

1. Žukienė, K., Jankauskaitė, V., Buika, G., Margelevičius, J. Surface and Interfacial Properties of Polychloroprene/ VeoVa blends. In: *Baltic Polymer Symposium BPS-2002*, ed.: Proceedings of Symposium 2002, Nida, September 18-20, 2002: pp. 134-139.
2. Žukienė K., Jankauskaitė V. Investigation of Adhesion Promoter Content on the Properties of Contact adhesives. In: *Baltic Polymer Symposium 2003*, ed.: Proceedings Symposium 2003, Jurmala, September 17-19, 2003: pp. 166-170.
3. Žukienė, K., Jankauskaitė, V., Fataraitė, E., Railaitė, A. Elastomerinių klijų modifikavimas įvairios struktūros vinilacetato dariniais. *Kn.*: Vartojimo reikmenų technologijos ir dizainas, *leid.*: Konferencijos pranešimų medžiaga, Kaunas, Technologija, 1999: pp. 26-29.
4. Navickaitė, K., Žukienė, K., Jankauskaitė, V., Railaitė, A. Vinilo dariniais modifikuoto polichloropreno savybių tyrimas. *Kn.*: Vartojimo reikmenų technologijos ir dizainas, *leid.*: Konferencijos pranešimų medžiaga, Kaunas, Technologija, 2000: pp. 3-8.
5. Merkevičienė, J., Žukienė, K., Fataraitė, E., Jankauskaitė, V. Klijų modifikavimo VeoVa polimeriais galimybė. *Kn.*: Vartojimo reikmenų technologija ir dizainas. *leid.*: Konferencijos pranešimų medžiaga. Kaunas, Technologija, 2002: pp. 3-8.

Information About the Author of Dissertation

1992 – 1996: bachelor's degree studies at Kaunas University of Technology, Faculty of Design and Technologies; Bachelor of Science in Industrial Engineering.

1996 – 2000: master's degree studies at Kaunas University of Technology, Faculty of Design and Technologies; Master of Science in Industrial Engineering.

2000 – 2004: doctoral's degree studies at Kaunas University of Technology, Faculty of Design and Technologies.

Reziumė

Tiriamoji problema. Adhezinių reiškinių vertinimo teorijų yra daug, tačiau universalios, galinčios paaiškinti adhezinio ryšio susidarymo mechanizmą, nėra. Todėl, kuriant adhezinės kompozicijas, šiuo metu egzistuojančiomis adhezinių reiškinių vertinimo hipotezėmis pasinaudoti sudėtinga. Šio reiškinio stadijiškumas ir daugelio veiksnių įtaka apsunkina adhezinio sujungimo formavimosi ir elgsenos bendrą dėsningumą nustatymą. Adhezinio sujungimo stiprumas priklauso nuo daugelio tarpusavyje susijusių veiksnių. Jį lemia ne tik adhezinės, bet ir mechaninės ar energetinės kompozicijos komponentų savybės. Todėl naujų adhezinių reiškinių vertinimo kriterijų paieška, eksperimentinių duomenų kaupimas ir analizė leistų suformuluoti teiginius, kurie palengvintų medžiagų adhezinio pajėgumo ar sanklijų stiprio prognozavimą.

Darbo aktualumas. Platus polimerų mišinių panaudojimas įvairiose srityse, siekiant gauti medžiagas, pasižyminčias tam tikru iš anksto pageidaujamu savybių kompleksu bei išvengti naujų medžiagų sintezės, lemia tokių medžiagų mokslinių tyrimų aktualumą. Polimerų mišinių išskirtinumą sąlygoja ne tiesinis, o sinergetinis savybių kitimo pobūdis, kuris yra jų unikali dvifazės struktūros rezultatas. Besiskiriančių savybėmis fazių darinys turi kitokias nei išeitinių mišinio komponentų savybes. Tačiau polimerų mišinių savybių prognozavimą apsunkina daugelio parametrų įtaka jų struktūrai. Didelę įtaką mišinių struktūrai daro dispersinės fazės parametrai, tarpfazinio sluoksnio struktūra, sąveikos tarpfazinėje riboje intensyvumas, maišomų polimerų savybės bei gamybos sąlygos. Todėl vienas iš pagrindinių polimerų mišinių tyrimo uždavinių yra ryšio tarp mišinių formavimosi mechanizmo, jų morfologijos ir savybių nustatymas.

Šiuo metu didelis dėmesys skiriamas tarpfazinių ir paviršinių reiškinių įtakos polimerų mišinių savybėms analizavimui. Tai pagrįsta tuo, kad paviršinių mišinio sluoksnių formavimosi ypatumų bei savybių tyrimai leidžia numatyti procesus, vykstančius polimerų adhezinės sąveikos metu, bei kitus reiškinius, kuriems yra svarbios ribinių sluoksnių struktūra ir savybės.

Moksliniuose darbuose dominuoja polimerų lydalu mišinių morfologijos ir savybių tyrimai. Tuo tarpu darbų, nagrinėjančių trikomponentes *polimeras-polimeras-tirpiklis* sistemų savybes, yra gerokai mažiau. Šių tyrimų stoka gali būti tolimesnių tyrimų akstinas.

Darbo tikslas. Ištirti modifikuotų polichlorpreninių adhezinių kompozicijų morfologijos kitimo dėsningumus, siekiant prognozuoti sanklijų adhezinę ir mechaninę elgseną, norint gauti gerų eksploatacinių savybių gaminius.

Šiam tikslui pasiekti buvo iškelti tokie **uždaviniai**:

- ištirti polichlorpreninių klijų modifikavimo polimeriniais priedais galimybes;
- įvertinti modifikuotų klijų struktūros įtaką jų savybėms;

- ištirti polichlorpreno bei modifikuojančių polimerinių priedų paviršiaus įtempius;
- nustatyti polimerinio priedo paviršinių savybių įtaką polichlorpreninių klijų struktūrai;
- įvertinti modifikuotų polichlorpreninių klijų komponentų sąveikos parametrus bei suderinamumą.

Darbo mokslinis naujumas ir praktinis vertingumas. Naudojant įvairios prigimties polimerinius priedus galima pagerinti adheziųjų kompozicijų savybes. Nustatyta, kad įvairūs versatinės rūgšties vinilo esterio dariniai, butadiennitriliniai ar izopreniniai kaučiukai, polimetilmetakrilatas gali būti naudojami kaip efektyvūs polichlorpreninių klijų modifikatoriai, gerinantys technologines ir eksploatacines jų savybes.

Įvertinta modifikuotų klijų sudėties, struktūros ir polimerinio priedo prigimties įtaka jų savybėms:

- nagrinėti polichlorpreninių tirpiklinių klijų plėvelės struktūros formavimosi mechanizmai, struktūros pokyčius vertinant pagal adhezinės kompozicijos fazes sudarančių polimerų bei jų mišinių klampų vertes;
- modifikuotų polichlorpreninių kompozicijų fazių elgsena buvo aiškinama, naudojantis dispersinės fazės dalelių skilimo ir koalescencijos procesų modeliais. Nagrinėta dispersinių dalelių pasiskirstymo pagal dydį funkcijos priklausomybė nuo mišinio sudėties, maišymo parametrų ir fazes sudarančių polimerų klampų santykio;
- polimerų plėvelių paviršiaus įtempiai bei poliškumas įvertintas teoriniais ir eksperimentiniais metodais, parodyti šių metodų trūkumai ir privalumai;
- nustatyta maišomų komponentų paviršiaus įtempių įtaka kompozicijos adhezinėms savybėms;
- ištirta adhezinės kompozicijos suderinamumo bei sąveikos tarpfazinėje riboje įtaka polichlorpreninių klijų savybėms.

Atlikti moksliniai tyrimai gali būti pritaikyti prognozuojant adheziųjų kompozicijų savybes, o nustatyti dėsningumai gali padėti kryptingai parinkti komponentus, kad būtų gaunamos adhezinės kompozicijos su norimu savybių kompleksu. Nustatyti dėsningumai svarbūs ne tik praktiniu, bet ir moksliniu požiūriu.

Išvados

1. Polichlorpreninių klijų savybes galima gerinti modifikuojant juos įvairiais polimeriniais priedais, tokiais kaip versatinės rūgšties vinilo esterio (Veova), stireno dariniais. Klijų savybes keičia ir butadiennitriliniai ar izopreniniai kaučiukai bei polimetilmetakrilatas. Nustatyta, kad šiais priedais modifikuotiems polichlorpreniniams klijams pasireiškia sinergizmo efektas, kurio laipsnis priklauso nuo priedų prigimties ir kiekio.

2. Geriausiomis savybėmis pasižymi polichlorpreniai klėjai, modifikuoti nedideliais (3 mas.% - 10 mas.%) VeoVa kopolimerų kiekiais. Sanklių stipris, klijų plėvelių tamprumo modulis ir tirpalo klampa padidėja 30 % - 70%. Nustatyta, kad klijų savybių kitimas susijęs su struktūros, komponentų suderinamumo bei sąveikos tarpfazinėje riboje pokyčiais. Optimalios šiais kopolimerais modifikuotų polichlorpreninių klijų savybės gaunamos tuomet, kai kompozicija turi suspensinę struktūrą.
3. Modifikuotų polichlorpreninių klijų reologinės savybės priklauso nuo jų struktūros. Klijų klampos sumažėjimas, esant nedideliems VeoVa ir PSK kopolimerų kiekiais (1 mas.% - 2 mas.%), gali būti susijęs su smulkiadispersinės suspensinės struktūros susiformavimu bei silpna sąveika fazių skiriamosioje riboje. Didėjant dispersinę fazę sudarančio kopolimero kiekiui (iki 5 mas.% - 15 mas.%) dalelių dydis, sąveika fazių skiriamosioje riboje bei polichlorpreninių klijų klampa didėja. Toliau didėjantys kopolimerų kiekiai formuoja inversinę struktūrą, todėl sąveika tarpfazinėje riboje silpnėja, o klijų klampa mažėja.
4. VeoVa kopolimerais modifikuotų polichlorpreninių klijų struktūra priklauso nuo mikroreologinių procesų, vykstančių kompozicijos paruošimo ir klijų plėvelės formavimosi metu – kopolimerų dalelių skilimo ir koalescencijos. Dalelių stabilumą įvertinus pagal kapilario skaičiaus vertes, nustatyta, kad, esant mažam VeoVa kopolimero kiekiui (3 mas.%), dalelės yra stabilios būsenos, nes yra per mažos, kad vyktų jų skilimas, ir per toli viena nuo kitos, kad vyktų jų koalescencija. Didėjant kopolimero kiekiui iki 20 mas.%, vyksta ir dalelių skilimas, ir jų koalescencija, todėl dalelių spindulys ir kompozicijos polidispersiškumas didėja.
5. Nustačius polichlorpreno ir modifikuojančių priedų plėvelių paviršines savybes gauta, kad VeoVa polimerai ir kopolimerai yra mažo paviršiaus įtempio medžiagos. Tuo tarpu piperileno stireno kopolimero paviršiaus įtempio vertė yra žymiai didesnė nei kitų polimerinių medžiagų. Tačiau tirtų polimerų paviršiaus įtempio vertės priklauso nuo pasirinkto (eksperimentinio arba/ir teorinio) įvertinimo metodo. Eksperimentiniai metodai, paremti vilgymo kampo matavimu, priklauso nuo darbe naudojamų paviršiaus įtempių skaičiavimo lygčių ir skysčių prigimties. Teoriniais metodais gautos tirtų polimerų paviršiaus įtempių vertės sutampa su vertėmis, nustatytomis eksperimentiniu būdu, bet jos neparodo įtempių priklausomybės nuo polimero molekulinės masės.
6. Modifikuotų polichlorpreninių klijų plėvelių paviršiaus įtempių bei paviršiaus morfologijos tyrimai, atlikti atominių jėgų mikroskopu, parodė, kad tirtų polimerinių priedų paviršiaus įtempių vertės turi didelę įtaką polichlorpreninių kompozicijų adhezinėms savybėms bei struktūrai:

- VeoVa kopolimerai, turintys panašų kaip polichlorprenas paviršiaus įtempį, didelės įtakos jo paviršiaus savybėms nedaro. Šiais kopolimerais modifikuotų adhezinių kompozicijų savybių pokyčiai priklauso nuo komponentų suderinamumo ir morfologijos;
 - VeoVa polimeras, pasižymintis mažesniu nei polichlorprenas paviršiaus įtempiu, koncentruojasi plėvelės paviršiuje, šitaip mažindamas kompozicijos paviršiaus įtempio vertes bei gerindamas klijų adhezinės savybes;
 - didesnės už polichlorpreno piperileno stireno kopolimero paviršiaus įtempio vertės lemia klijų plėvelės išsisluoksniavimą jos formavimosi metu. Piperileno stireno kopolimeras migruoja į apatinį klijų plėvelės sluoksnį ir didina sąveiką tarp mažo paviršiaus įtempio substrato ir polichlorpreninių klijų.
7. Modifikuotų polichlorpreninių klijų suderinamumas, įvertintas kompozicijos komponentų makromolekulių sąveikos parametrais, nustatytais viskozimetriniu praskiestų tirpalų metodu. Gauta:
- polichlorprenas ir VeoVa-11/MMA/2EHA kopolimeras dėl stūmos jėgų, veikiančių tarp jų makromolekulių, yra nesuderinami nepriklausomai nuo jų santykio kompozicijoje;
 - polichlorprenas yra suderinamas su VeoVa polimeru tik esant didesniems šio priedo kiekiams (9 mas% - 15 mas.%). Priklausomai nuo VeoVa polimero kiekio, kompozicijoje pasireiškia tiek stūmos, tiek ir traukos jėgos;
 - piperileno stireno kopolimeras yra suderinamas su polichlorprenu visame tirtame kompozicijos intervale. Toks suderinamumo kitimas yra susijęs su traukos jėgų, veikiančių tarp atskirų kompozicijų komponentų makromolekulių, veikimu.
8. Parodyta, kad paviršiaus įtempis gali būti vienas iš adhezinių kompozicijų komponentų parinkimo kriterijų: tarpusavio paviršiaus įtempio įvertinimas leidžia prognozuoti komponentų suderinamumą, struktūros formavimąsi, adhezinės ir eksploatacinės savybes.

UDK 665.93:620.18(043)

SL 344. 2004-12-9. 1 leidyb. apsk. 1. Tiražas 70 egz. Užsakymas 452.
Išleido leidykla „Technologija“, K. Donelaičio g. 73, 44029 Kaunas
Spausdino leidyklos „Technologija“ spaustuvė, Studentų g. 54, 51424, Kaunas